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Mechanical Properties of Electrochemically Prepared Polypyrrole Films

The mechanical and conducting properties of free-standing films of polypyrrole toluenesulfonate depend on the preparation conditions. Films prepared in aqueous ethylene glycol solvent mixtures show a variation of two orders of magnitude in the conductivity and of a factor of three in the tensile strength.

Introduction

Since the initial report on the availability of conducting polypyrrole film via the electrochemical oxidation of pyrrole [1], numerous reports have appeared describing the use of this material in electrode applications [2–12]. The interest in these thin films arises from the fact that they are easily prepared, adherent to supporting electrodes, electroactive, and quite stable to a variety of conditions [13]. It is noteworthy that all of the applications considered address only the thin polymer film attached to the electrode where it was generated, and not the thicker free-standing films. Thin films of polypyrrole (≈40 nm) are electroactive and electrochromic [2, 13], and have been considered for display and ion gate applications [3]. They have also been considered as passivation layers (for protection of semiconductor electrodes against photocorrosion) in solar cells [5–12].

As for the thicker, free-standing films, it is the film in the oxidized form which is easier to handle, since it is in its stable form. Correspondingly, it is this form which has electrical conductivity. While the neutral form is easily prepared by adjusting the polarity of the electrodes in the preparation procedure after the film has been formed [1, 2], the neutral film is less interesting because it is an unstable insulator. Before any real interest is developed in the use of the conducting free-standing films in technical applications, it must be demonstrated both that the films are stable and that they have good mechanical properties. In this paper we present the results of our study and describe the influence of the preparation conditions on the conductivity and mechanical properties of free-standing polypyrrole films. This paper is not intended as a complete review of these films and all their derivatives, their properties, or the preparative procedures. These topics have been reviewed elsewhere [13–15].

Film preparation

Polypyrrole films are prepared electrochemically by the oxidation of commercially available pyrrole. The polymer produced in this reaction remains on the electrode as an insoluble, electrically conductive film. These films can be conveniently prepared in a one-compartment cell equipped with a platinum working electrode, a gold counter electrode, and a calomel reference electrode. The amount of film produced in a given preparation, or the film thickness if the effective area of the working electrode is known, can be controlled by monitoring the electrical current. This control is possible because the electropolymerization reaction has electrochemical stoichiometry; ≈2.2 electrons pass per molecule of pyrrole reacted [13, 14].

The rate of film growth depends directly on the current density and, at least for thinner films, it has a linear dependence on time [16]. As may be expected, the current

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density varies with the resistance of the electrolytic solution, the concentration of the pyrrole, and the applied voltage [17].

The films described in this work were prepared in solutions containing 0.2 M pyrrole and 0.1 M tetraethylammonium toluenesulfonate, which had been purged with helium prior to electrolysis. The solutions were electrolyzed using a potential of 0.8–1.3 V until the films were 15–35 μm thick. The films prepared at these potentials had reasonable mechanical properties. Higher voltages were not used in order to avoid the intervention of undesirable reactions, while films prepared at potentials less than 0.8 V had poor mechanical properties. The films were prepared using "quiet" solutions since stirring did not affect the rate of film growth.

The actual time involved per film preparation depends on the electrode area used. As an example, when a 12.5% water-12.5% ethylene glycol-75% acetonitrile solution was used, a 20-μm film formed on a 15.6-cm^2 (2.5-in.^{2}) surface in ≈15 min using 1.2 V. The films were removed from the electrode, rinsed with acetonitrile, and dried in air.

Conductivities and mechanical properties

The measured conductivities and mechanical properties for polypyrrole toluenesulfonate (PPTS) films are summarized in Table 1. The measurements were performed using a Veeco four-point-probe contact instrument and an Instron mechanical tester. The values given in the table represent the average of two to five measurements, unless otherwise noted.

The conductivity and mechanical strength of the films can be made to vary with the addition of water or ethylene glycol to the electrolyte solution. Of these, water has the greater effect. With increasing amounts of water added as a co-solvent, the conductivity of the films decreases by more than two orders of magnitude. The minimum value occurs when the films are prepared in a 1:3 water-acetonitrile solution; see Fig. 1.

In general, the films are hard and strong, and they break at small elongations (≈4–8%). Films with good mechanical properties are produced in solutions containing up to 25% water plus 25% ethylene glycol. The conductivities of these films again decrease to a minimal value with increasing amounts of water and ethylene glycol in the solution. The least conducting films are formed in 12.5% water-12.5% ethylene glycol-75% acetonitrile solutions. The origin of these changes is not known but may be related to the disruption of the extended π structure in the better (i.e., more polar) solvating mixtures. It is not the result of a gross structural change, such as the degree of oxidation of the polymer, because the elemental analyses of the materials indicate the same ratio of polymer to toluenesulfonate anion for the two films that have widely different conductivities. These results are listed in Table 2.

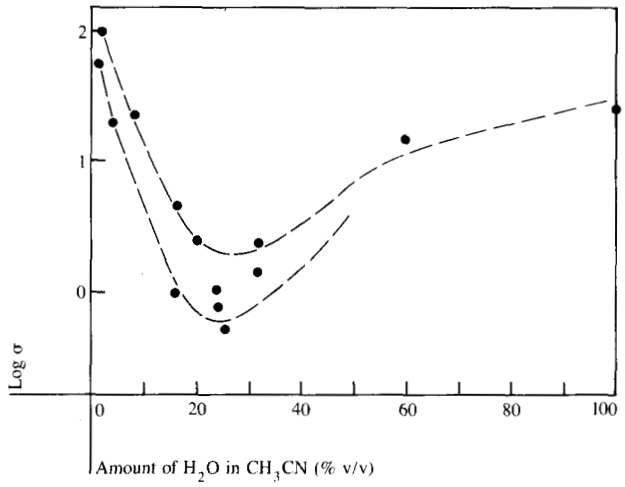

Figure 1 Dependence of conductivity values of two 30-μm-thick polypyrrole toluenesulfonate films prepared in electrolyte solutions containing varying amounts of water. The minimum conductivity was obtained when films were prepared in a 1:3 water/acetonitrile solution.

Table 1 Polypyrrole toluenesulfonate films prepared in various acetonitrile (ACN)-co-solvent systems; EG = ethylene glycol, G = glycerol. Numbers given in parentheses after the solvent are the percentage of listed co-solvents. Note: 1 Pa ≈ 6895 psi.

Co-solvent	*Conductivity* (Ω^{-1}-cm^{-1})	*Tensile strength* (psi)	*Elongation at break* (%)	*Young's modulus* (psi)
H_2O-ACN				
(1:99)	60–100	8600	4	0.35
(1:99)	30	6200	17	0.12
(25:75)	0.5	1200	4	0.07
EG-ACN				
(25:75)	25	4750	5	0.16
(50:50)	29	7210	8	0.13
H_2O-EG-ACN				
(1:1:98)	40	7350	8	0.20
(2:5:93)	8	6130	8	0.15
(5:5:90)	4–17	5900	14	0.13
(12.5:12.5:75)	0.5–2	5090	7	0.12
(25:25:50)	3	5310	6	0.15
H_2O-EG				
(50:50)	17	2700	6	0.05
G-ACN				
(1:99)	14	5550	8	0.19
G-H_2O				
(50:50)	19	8340	6	0.24

Table 2 Elemental analyses (given as atom mole ratios); the values given have been normalized to nitrogen (N).

Preparation solution	*Polymer*			*Anion*				*Balance*
	C	*H*	*N*	*C*	*H*	*S*	*O*	
H_2O-ACN (1:99)	4.00	3.60	1.0	2.51	2.51	0.32	1.96	97.71
EG-H_2O-ACN (12.5:12.5:75)	4.00	3.00	1.0	2.47	2.47	0.28	1.46	101.21

Table 3 Mechanical properties of some polymers. Note: 1 Pa ≈ 6895 psi.

Material	*Tensile strength* (psi)	*Elongation at break* (%)	*Young's modulus* (psi)
Polypyrrole toluenesulfonate (60–100 Ω^{-1}-cm^{-1})	8600	4	0.35
Phenol formaldehyde (type G)	8000	1.0–1.5	0.90
Melamine formaldehyde	8000	0.5	1.20
Polystyrene	7000	3	0.50
Poly(methyl methacrylate)	8000	5	0.40
Polyesters	6000	5–300	0.30
Polyethylene	1800	550	0.20
Polytetrafluoroethylene	2000	100	0.50

Table 4 Properties of polypyrrole tetrafluoroborate (PPTF) and polypyrrole perchlorate (PPPC) films prepared in various acetonitrile-co-solvent systems; EG = ethylene glycol; G = glycerol; numbers given in parentheses are the percentages of the co-solvents. Note: 1 Pa ≈ 6895 psi.

Polymer	*Co-solvent*	*Conductivity* (Ω^{-1}-cm^{-1})	*Tensile strength* (psi)	*Elongation at break* (%)	*Young's modulus* (psi)
PPTF	H_2O-ACN (1:99)	30–60	6430	5	0.16
	H_2O-EG (50:50)	16–30	2030	3	0.10
	G-ACN (1:99)	25	2000	3	0.08
PPPC	H_2O-ACN (1:99)	55–90	6130	5	0.17
	H_2O-EG (5:5:95)	28	3720	4	0.12

The mechanical properties of these films compare quite well with the properties of polystyrene and poly(methyl methacrylate) (PMMA). This result is unexpected, since the materials are very different. The polypyrrole films are composite materials in which the polymer chains have an unsaturated backbone structure that is cationically charged and that has strong intermolecular interactions with the anions and neighboring polymer chains. On the other hand, the PMMA films are not composites. They are neutral and have a linear saturated backbone structure containing pendant unsaturated groups which have some π-π interactions. The properties of these materials are compared in Table 3 [18].

The polypyrrole films are less stretchable than fully saturated linear polymers such as polyethylene and polytetrafluoroethylene. They are also less rigid than cross-linked aromatic polymers such as phenol formaldehyde and melamine formaldehyde (Table 3).

The effect observed with ethylene glycol should be similar for many glycols. In order to test this, three other glycols were investigated: 1,2-propanediol, 1,3-propanediol, and 1,4-butanediol. Films prepared in solutions containing 12.5% 1,3-propanediol or 1,4-butanediol-12.5% water-75% acetonitrile were found to have conductivities of 0.3 Ω^{-1}-cm^{-1}. The

film prepared using 1,4-butanediol had a tensile strength of 24 MPa (3500 psi), a 4–7% elongation at break, an initial yield value of 19 MPa (2800 psi), and a Young's modulus of 0.6 kPa (0.09 psi). The film prepared using 12.5% 1,2-propanediol-12.5% water-75% acetonitrile had a conductivity of 4 Ω^{-1}-cm^{-1}, a tensile strength of 39 MPa (5700 psi), a 7% elongation at break, an initial yield value of 32 MPa (4600 psi), and a Young's modulus of 0.7 kPa (0.1 psi). Thus, films with reasonably good properties can be prepared using both linear and branched glycols. The effect of varying the relative amounts of co-solvent on the properties of the films was not determined. In principle, a wide variety of linear and branched glycols should be useful as co-solvents for the preparation of these films.

Glycerol as a co-solvent also changes the properties of the films, as can be seen in Table 4. It is, however, poorly miscible with the electrolyte solutions, which severely limits its use.

Physical characteristics and composition

The films prepared in 12.5% ethylene glycol-12.5% water-75% acetonitrile solutions resemble the films produced in acetonitrile solutions, even though the former are a hundred times less conducting. Scanning electron micrographs (SEMs) of the growing surface closely resemble previously reported micrographs of polypyrrole film surfaces [15]; see Figs. 2(a) and 2(b). The films have a flotation density of 1.36 g/cm^3, which is essentially the same as the density of the films grown in acetonitrile containing 1% water, 1.37 g/cm^3 [15].

The elemental analysis of the films, after washing with copious amounts of acetonitrile, indicates that the films consist of 56% pyrrole polymer and 44% toluenesulfonate anion. The atom mole ratios provided by the analysis are listed in Table 2, along with the values for the films prepared in acetonitrile containing 1% water. The results are consistent with a polymer structure composed of linearly attached pyrrole units, as previously proposed. The pyrrole polymer contains 0.28 cationic charges for every pyrrole unit; it attains charge neutrality by affiliating with the toluenesulfonate anion. The most striking aspect of these results is that there is no evidence that ethylene glycol is contained in the film. Yet the ethylene glycol in the preparation mixture clearly alters the properties of the resulting film. Therefore, to the extent that the glycol is originally present in the film, it is easily removed in the washing process. It must not be chemically bound to the polymer. The role of the solvent in the electropolymerization process must be very important. There appears to be some form of specific solvation which stabilizes the π-segments of intermediate length along the polymer chain.

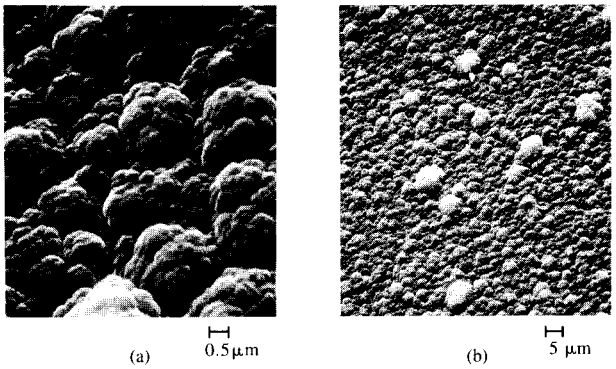

Figure 2 Scanning electron micrographs of a polypyrrole toluenesulfonate film prepared in a 1:1:6 ethylene glycol/water/acetonitrile solution at two different magnifications. Bar scale values are (a) 0.5 μm and (b) 5 μm. The structure closely resembles previously reported micrographs of polypyrrole film surfaces (see text).

Film stability

The polypyrrole toluenesulfonate films appear to remain fairly stable while stored under ambient conditions. Films which were left standing in air for nine weeks appeared physically unchanged. The conductivities, however, increased by ≈25% in every case, while there was no significant change in the mechanical properties. After 27 months two films with conductivities of 50 and 7 Ω^{-1}-cm^{-1} had conductivities of 7 and 1 Ω^{-1}-cm^{-1}, respectively, while one film with a conductivity of 1 Ω^{-1}-cm^{-1} remained unchanged.

As previously reported [15], the conductivities of these films increase with temperature prior to final irreversible decomposition of the films. In addition, both the magnitude of the change in the conductivity and the decomposition temperature depend on the anion in the film. In the case of polypyrrole toluenesulfonate, films prepared with the higher conductivities (50 Ω^{-1}-cm^{-1}) reveal an ≈70% increase in conductivity before decomposing at 160°C. The thermal gravimetric analysis (TGA) of these films in a nitrogen atmosphere shows a weight loss beginning at 180°C and increasing to 10% at 260°C (Fig. 3). The corresponding differential scanning calorimeter (DSC) trace shows peaks for endothermic reactions at 150° and 330°C. The less-conducting films (4 Ω^{-1}-cm^{-1}) show an increase of a factor of 3.5 in conductivity before decomposing at 280°C. The TGA of these films shows a weight loss beginning at 190°C and increasing to 10% at 285°C. The corresponding DSC trace for this material increases fairly linearly up to 400°C, with a small deflection due to an endothermic reaction visible at 130°C. The less-conducting films, which showed high sensitivity to temperature, were also analyzed for thermomechanical stability. In this analysis, the penetration of a probe of known weight into the film is measured as a function of temperature. The thermomechanical analysis traces for two

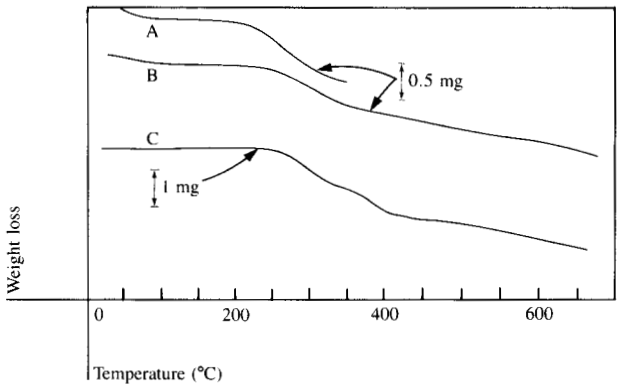

Figure 3 Thermal gravimetric analysis of polypyrrole toluenesulfonate films prepared in acetonitrile solutions containing (Curve A) 1% water, (Curve B) 25% water-25% ethylene glycol, and (Curve C) 12.5% water-12.5% ethylene glycol.

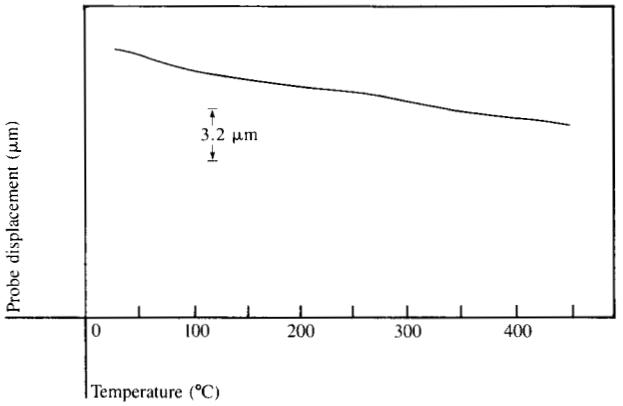

Figure 4 Thermomechanical analysis of polypyrrole toluenesulfonate film (temperature corrected for chromel alumel thermocouples).

films prepared in 12.5% water-12.5% ethylene glycol-75% acetonitrile show a fairly smooth gradual decrease between 25° and 450°C, with an initial slope of 0.019 μm/° and a small deflection at ≈270°C (Fig. 4). This deflection is probably produced by the same chemical degradation process of the film. The overall slope is 0.011 μm/°, with 14% and 29% shrinkages occurring at 280° and 450°C, respectively. The amount of temperature-dependent film shrinkage is much less than the observed increase in conductivity. Therefore, the principal change in the conductivity must be due to factors other than the dimensional changes in the film.

Other anions

Because the anion makes up ≈40% of the weight of the polymeric films, it is not unreasonable to expect variations in the properties of the films due to the anion. We previously reported how films which were prepared under the same set of conditions, where the only variation was the choice of the anion of the electrolyte, could have variations in the conductivity by two orders of magnitude [15]. Variation of the anion also produces a small change in the flotation density of the films, very dramatic changes in the topology of the growing surfaces, and some changes in the stability and conductivity of the films upon heating. It is likely that these variations result from the chemical nature of the anion, and not from changes in the stoichiometry of the films, since the ratio of the anion to pyrrole units in the films remains in the narrow range of 0.25 to 0.33 [15].

The films which contained tetrafluoroborate and perchlorate anions are found to be weaker than, although just as hard as, films containing toluenesulfonate anions (see Table 4). Although all of the films in this comparison have similar conductivities and elongation and modulus values, the former have tensile strengths which are 30–40% lower.

The films containing tetrafluoroborate and perchlorate anions are less stable than the films containing toluenesulfonate anions. As mentioned, the films decompose irreversibly at temperatures above 150°C. After they had been stored in ambient conditions for nine weeks, the conductivity of both of these films was reduced by ≈50%.

Conclusions

Our results show that electrochemically deposited films of polypyrrole toluenesulfonate are quite stable in ambient conditions and have reasonably good mechanical properties. Although these films are ionic composites, their mechanical properties are analogous to those of the conventional polypyrrole polymers.

Acknowledgments

The authors wish to thank C. Wilbur, F. Anger, H. Acedo, J. Carothers, M. Krounbi, A. Logan, and T. Smith for their help with the various aspects of this work.

References

1. A. F. Diaz and J. I. Castillo, "A Polymer Electrode with Variable Conductivity: Polypyrrole," *J. Chem. Soc., Chem. Commun.*, No. 9, 397–398 (1980).
2. A. F. Diaz, Juan I. Castillo, J. A. Logan, and Wen-Yaung Lee, "Electrochemistry of Conducting Polypyrrole Films," *J. Electroanal. Chem.* **129,** 115–132 (1981).
3. P. Burgmayer and R. W. Murray, "An Ion Gate Membrane: Electrochemical Control of Ion Permeability through a Membrane with an Embedded Electrode," *J. Amer. Chem. Soc.* **104,** 6139–6140 (1982).
4. A. Diaz, J. M. Vasquez Vallejo, and A. Martinez Duran, "[Pt]Polypyrrole: A New Organic Electrode Material," *IBM J. Res. Develop.* **25,** 42–50 (1981).
5. Randy A. Bull, Fu-Ren F. Fan, and Allen J. Bard, "Polymer Films on Electrodes. VII. Electrochemical Behavior at Polypyr-

role-Coated Platinum and Tantalum Electrodes," *J. Electrochem. Soc.* **129,** 1009–1015 (1982).
6. Rommel Noufi, Dennis Tench, and Leslie F. Warren, "Protection of n-GaAs Photoanodes with Photoelectrochemically Generated Polypyrrole Films," *J. Electrochem. Soc.* **127,** 2310–2311 (1980).
7. Rommel Noufi, Arthur J. Frank, and Arthur J. Nozik, "Stabilization of n-Type Silicon Photoelectrodes to Surface Oxidation in Aqueous Electrolyte Solution and Mediation of Oxidation Reaction by Surface-Attached Organic Conducting Polymer," *J. Amer. Chem. Soc.* **103,** 1849–1850 (1981).
8. Terje Skotheim, Ingemar Lundström, and Jiri Prejza, "Stabilization of n-Si Photoanodes to Surface Corrosion in Aqueous Electrolyte with a Thin Film of Polypyrrole," *J. Electrochem. Soc.* **128,** 1625–1626 (1981).
9. T. Skotheim, L.-G. Petersson, O. Inganäs, and I. Lundström, "Photoelectrochemical Behavior of n-Si Electrodes Protected with Pt-Polypyrrole," *J. Electrochem. Soc.* **129,** 1737–1741 (1982).
10. O. Inganas, T. Skotheim, and I. Lundström, "Schottky Barrier Formation Between Polypyrrole and Crystalline and Amorphous Hydrogenated Silicon," *Physica Scripta* **25,** 863–867 (1982).
11. Gerald Cooper, Rommel Noufi, Arthur J. Frank, and Arthur J. Nozik, "Oxygen Evolution on Tantalum-Polypyrrole-Platinum Anodes," *Nature* **295,** 578–580 (1982).
12. A. J. Frank and K. Honda, "Visible-Light-Induced Water Cleavage and Stabilization of n-Type Cadmium Sulfide to Photocorrosion with Surface-Attached Polypyrrole-Catalyst Coating," *J. Phys. Chem.* **86,** 1933–1935 (1982).
13. A. F. Diaz and K. K. Kanazawa, "Polypyrrole: An Electrochemical Approach to Conducting Polymers," *Extended Linear Chain Compounds*, J. S. Miller, Ed., Vol. 3, Plenum Press, New York, 1982, pp. 417–447.
14. A. F. Diaz, "Electrochemical Preparation and Characterization of Conducting Polymers," *Chemica Scripta* **17,** 145–148 (1981).
15. M. Salmon, A. F. Diaz, A. J. Logan, M. Krounbi, and J. Bargon, "Chemical Modification of Conducting Polypyrrole Films," *Mol. Cryst. Liq. Cryst.* **83,** [1297–1308] 265–276 (1982).
16. E. M. Genies, G. Bidan, and A. F. Diaz, "Spectroelectrochemical Study of Polypyrrole Films," *J. Electroanal. Chem.* (1983, in press).
17. Jiri Prejza, Ingemar Lundström, and Terje Skotheim, "Electropolymerization of Polypyrrole in the Presence of Fluoroborate," *J. Electrochem. Soc.* **129,** 1685–1689 (1982).
18. A. E. Lever and J. Rhys, in *The Properties and Testing of Plastic Materials*, Chemical Publishing Co., New York, 1962, p. 30.

Received January 6, 1983

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